PHYSICAL REVIEW VOLUME 126, NUMBER 3 MAY 1, 1962

Paramagnetic Resonance of Trivalent Fe^{57} in Zinc Oxide*

W. M. WALSH, JR., AND L. W. RUPP, JR.
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received December 21, 1961)

Tetrahedrally-coordinated trivalent iron has been found to be a common impurity in flux-grown crystals of zinc oxide. The room temperature paramagnetic resonance spectrum of isolated ions may be described by a conventional axial spin Hamiltonian with parameters: $g=2.0060\pm0.0005$, $D=-(594\pm1)\times10^{-4}$ cm^{-1}, $F=(4\pm5)\times10^{-4}$ cm^{-1}, $a=(39\pm5)\times10^{-4}$ cm^{-1}. Lines due to iron ions with nearby charge compensation (Li^+ ions) have also been observed. The magnitude of the cubic field parameter (a) is discussed. The hyperfine coupling constant of Fe^{57} in an enriched sample is $|A|=(9.02\pm0.2)\times10^{-4}$ cm^{-1} which is of interest in connection with Robert's nuclear resonance measurements of sublattice magnetizations in yttrium-iron garnet. It appears likely that both sublattices are aligned within 1% at very low temperatures.

INTRODUCTION

TRIVALENT iron has been observed several times with paramagnetic resonance (PMR) techniques in octahedral coordination[1] but has been reported only once previously in tetrahedral coordination.[2] In the course of a PMR survey of tetrahedral compounds we have observed Fe^{3+} as a trace impurity in several crystals of ZnO. The spectrum is here reported and discussed with particular regard to the strength of the cubic component of the crystalline field and to the hyperfine coupling of Fe^{57} which is of importance in determining the degree of alignment of the d sublattice in yttrium-iron garnet.

1. SAMPLES AND APPARATUS

Single crystals of ZnO have been grown from fluxes[3] of molten lead fluoride by R. C. Linares, Jr., of these laboratories. In many cases iron-group impurities have been purposely added in the flux.[4] We have also added iron by diffusion from Fe_2O_3 powder surrounding ZnO crystals at ~800°C.

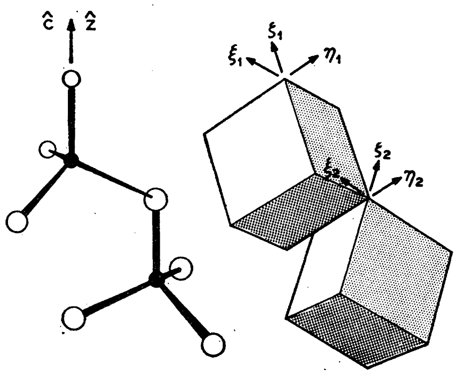

FIG. 1. The sketch at the left indicates the two types of metal ion sites in the wurzite structure. They differ in the azimuthal orientation of the cubic axes as shown at the right.

The room-temperature conductivity of these samples is usually high enough to cause excessive microwave loss. Addition of lithium to the initial melt or a subsequent baking of LiOH-coated crystals at 700° overnight results in very high resistivities[5] suitable for paramagnetic resonance (PMR) investigations. The spectrum of trivalent iron was observed in almost all samples, the highest concentrations (~10^{18} ions/cm^3) occurring in purposely doped material.

A conventional audio-frequency field-modulation spectrometer operating near 12 kMc/sec was used. Azimuthal rotation of the sample as well as polar rotation of the magnet permitted optimum orientation of the field relative to the crystal axes. Frequency measurements, both microwave and nuclear resonance (field determinations), were made with a Hewlett-Packard counter and associated heterodyning equipment. Provision was made for mercury lamp illumination of the sample in order to observe any effects of photoexcited carriers on the PMR spectra.

2. EXPERIMENTAL RESULTS

Zinc oxide has the hexagonal wurzite structure. Each metal ion is surrounded by an almost-regular tetrahedron of oxygen ions. The bond length along the hexagonal axis is slightly shorter than the other three (1.96 vs 1.98 Å). The metal site has trigonal symmetry (C_3) but there are two inequivalent sites related by a 60° rotation the about unique axis leading to overall hexagonal symmetry as indicated in Fig. 1. The crystalline electric field seen by the metal ion has a dominant component of cubic symmetry with a weaker trigonal component in addition.

The two sites are magnetically distinguishable in the case of Fe^{3+} paramagnetic resonance since the high spin of this ion ($S=\frac{5}{2}$) permits both quadrupolar and hexadecapolar fine structure splittings to be observed. The

---

* A preliminary report has been presented: W. M. Walsh, Jr., Bull. Am. Phys. Soc. **6**, 117 (1961).

[1] K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18. J. W. Orton, *Reports on Progress in Physics* (The Physical Society, London, 1959), Vol. 22.

[2] S. Geschwind, Phys. Rev. **121**, 363 (1961).

[3] J. W. Nielson and E. F. Dearborn, J. Phys. Chem. **64**, 1762 (1960).

[4] R. Pappalardo, D. L. Wood and R. C. Linares, Jr., J. Chem. Phys. **35**, 1460, 2041 (1961).

[5] J. J. Lander, J. Phys. Chem. Solids **15**, 324 (1960).

TABLE I. Spin-Hamiltonian parameters of Fe^{3+} in ZnO at room temperature.

g	2.0060 ± 0.0005
D	$-(593.7\pm1)\times10^{-4}$ cm^{-1}
F	$(4\pm5)\times10^{-4}$ cm^{-1}
a	$(39\pm5)\times10^{-4}$ cm^{-1}
$\|A\|$	$(9.02\pm0.2)\times10^{-4}$ cm^{-1}

spin Hamiltonian appropriate to axial (trigonal or higher) site symmetry is[2,6]

$$\begin{aligned}H={}&g\beta\mathbf{H}\cdot\mathbf{S}+D[S_z^2-\tfrac{1}{3}S(S+1)]\\&+(a/6)[S_\xi^4+S_\eta^4+S_\zeta^4-\tfrac{1}{5}S(S+1)(35^2+35-1)]\\&+(F/180)[35S_z^4-30S(S+1)S_z^2+25S_z^2\\&\qquad-6S(S+1)+35S^2(S+1)^2]\end{aligned}\qquad(1)$$

where ξ, η, and ζ refer to the cubic electric field axes and z refers to the trigonal axis. The distinction between the two types of sites in the wurtzite structure lies in the third (cubic) term of Eq. (1) since there are two sets of cubic axes (see Fig. 1).[7] This leads to doubling of the five-line spectrum for a general orientation of the magnetic field H with respect to the crystal axes. Figure 2 displays this doubling as a function of polar angle θ (angle between the field and the $\hat{c}$ or $\hat{z}$ axis) at the azimuth appropriate to maximum splitting (H in a plane defined by the hexagonal axis and a cubic field axis).

The parameters g, D, F, and a have been determined by numerical diagonalization of the secular determinant. Using the appropriate expressions given in reference 2, the magnitudes and relative signs of D and $a-F$ were obtained from the spectrum taken with H parallel to $\hat{c}$: $D=\pm593.7\times10^{-4}$ cm^{-1}, $a-F=\mp35.6\times10^{-4}$ cm^{-1}. A choice of signs was made on the basis of two assumptions: F is small in magnitude compared with D and a is positive. The reasons for these assumptions will be discussed in Sec. 3. It is thus inferred that D is negative. The secular equation was solved for a few compatible sets of values of a and F for several polar angles and two appropriate values of azimuth. A typical set of computed points is shown in Fig. 2. By plotting the calculated line splittings vs the chosen values of a and comparing with the experimental results it was possible to pick out an optimum value of a and hence of F. The final results are given in Table I. None of the parameters appears to be markedly temperature dependent though no very careful study was made. It would be desirable to observe the spectrum at very low temperatures (~1°K) in order to determine the sign of D directly. Our attempts to do this proved fruitless due to saturation of resonance transitions. No appreciable reduction in saturation could be achieved using the light from a high pressure mercury lamp (Osram HBO-200) focused (and filtered) by glass optics to excite photocarriers.

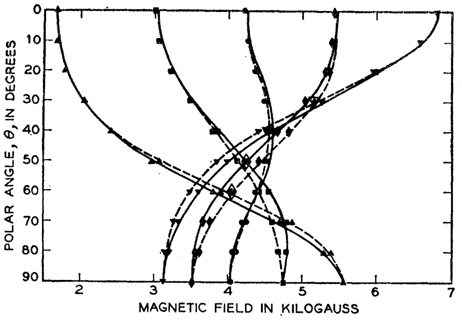

FIG. 2. Polar variation of the line positions in the paramagnetic resonance spectrum of Fe^{3+} in ZnO. The solid and dashed curves represent the experimental data taken at room temperature and 11.9 kMc/sec with the magnetic field in a plane containing the hexagonal axis (0°) and a cubic electric field axis (54°44′) of one site. The various points are computed as described in the text.

In addition to the relatively intense spectrum described above, a number of much weaker lines grouped near the central transition ($S_z=\frac{1}{2}\leftrightarrow-\frac{1}{2}$) were also observed. These lines are most clearly resolved when the applied field is parallel to the crystalline symmetry axis as shown in Fig. 3 where at least nine such peaks are seen. It is likely that they are the central lines of Fe^{3+} ions whose charge compensation (probably Li^+ ions since these are present in quantity) is localized within a few lattice constants of the magnetic ion.[8] Such local disturbances produce appreciably different and generally lower symmetry electric fields at the sites of corresponding iron ions; their PMR spectra thus differ from that of the effectively isolated Fe^{3+} ions.

Upon rotating the magnet slightly away from the hexagonal axis, the lines break up into triplets indicating there are three sites leading to each such transition. Due to the hexagonal symmetry of the crystal one would in general expect to find six equivalent spectra of each kind corresponding to the six possible equivalent sites for the compensating ion. In practice, only triplets are seen near the symmetry axis as the cubic field splitting which alone distinguishes between the two trigonal metal-ion sites vanishes as H approaches $\hat{c}$ (see Fig. 2). We have not attempted to study these charge-compensation spectra in detail since the angular variation are myriad and interference from the isolated-ion spectra is a serious difficulty. The fine structure lines corresponding to the central transitions have not been observed, presumably due to excessive line width (the fine structure satellites of the isolated-ion spectrum are several times broader than the central peak, as is usually the case in magnetic resonance since these transitions are more sensitive to low symmetry electric field components arising from strains, etc.).

---

[6] B. Bleaney and R. S. Treham, Proc. Roy. Soc. (London) **A223**, 1 (1954).

[7] This distinction has been discussed at length by C. Kikuchi and L. M. Mattarese, J. Chem. Phys. **33**, 601 (1960) for the case of Mn^{++} in calcite.

[8] Such charge-compensation spectra have been studied in the case of Cr^{3+} in MgO by J. E. Wertz and P. Auzins, Phys. Rev. **106**, 484 (1957).

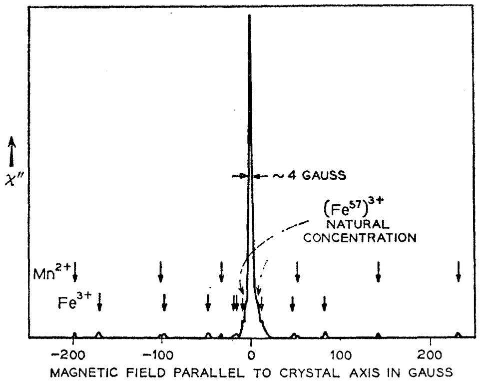

FIG. 3. Tracing of the PMR spectrum near the central line ($S_z=\frac{1}{2}\leftrightarrow\frac{1}{2}$) of the isolated-ion spectrum. Nine charge-compensation peaks are indicated as are six lines due to a trace of Mn^{2+}. The unresolved hyperfine structure of Fe^{57} in natural abundance is also seen.

Close perusal of the central isolated-ion transition discloses an unresolved "hump" on each side (see Fig. 3) which one suspects to be hyperfine structure arising from the 2% abundant isotope Fe^{57} whose spin is $I=\frac{1}{2}$ and whose moment is rather small.[9] The suspicion is confirmed upon diffusion-doping a relatively "clean" ZnO crystal from Fe_2O_3 powder enriched to ~60% abundance in Fe^{57}. The central transition for the sample is shown in Fig. 4 where the hyperfine structure is now quite well resolved. The corresponding electron-nuclear coupling term $A\mathbf{I}\cdot\mathbf{S}$ is easily evaluated since the separation of the outer lines in field is just $A/g\beta$ (see Table I).

3. DISCUSSION

A. Crystalline Field Parameters

The absolute magnitudes of the spin-Hamiltonian coefficients are of little present interest since no attmept will be made here to relate them to the detailed structure of the host crystal. Relative magnitudes are of some importance, however, particularly since we have inferred the relative signs of D and $a-F$ assuming $|F|$ to be small compared with $|D|$. The ansatz proved quite consistent (see Table I) and was based on the observed behavior of Fe^{3+} in other crystals[1,2] where $|D|:|F|$ ~50:1. It is perhaps remarkable that the fourth-order axial field coefficient F should prove so small in ZnO where the second-order parameter D is rather large.

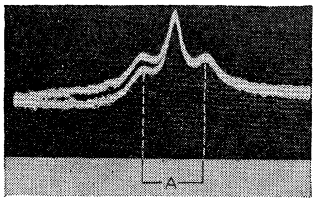

FIG. 4. The central transition of a sample doped with iron enriched to 60% in Fe^{57}. The hyperfine satellites are now resolved from the central Fe^{56} peak.

We have also assumed that the cubic crystalline field coefficient a is positive which is a plausible inference from Geshwind's work.[2] He found that the a parameters of Fe^{3+} in both the octahedral and the tertahedral sites of yttrium-gallium garnet were positive despite the change in sign of the cubic moment of the lattice potential at the two sites. Estimating the relative strengths of these potentials from a point-charge model Geschwind found that a for Fe^{3+} varied as the cubic potential Φ to the 2.2 power. Comparing our result for ZnO:Fe^{3+} with that of Low[10] for MgO:Fe^{3+} (octahedral) (in each case the trivalent iron occupies a normally divalent site so that polarization effects may be roughly comparable) we find $a\propto\Phi^{2.3}$. The agreement with Geschwind is excellent but both of these intercomparison experiments disagree with the observed variations of a for Fe^{3+} in MgO vs hydrostatic pressure[11] and temperature[12] which yield $a\propto\Phi^{4.25}$. Until a consistent experimental situation is attained, there is little point in discussing the relation of these results to recent theoretical treatments of S-state ions (see reference 2). It is possible that the attempt to correlate values of a on the basis of a point-charge approximation is seriously in error and that only a molecular-orbital formalism can properly account for the observations.[13]

B. Hyperfine Coupling

The isotropic interaction getween the magnetic electrons and the nucleus of an iron-group ion is generally held to be the result of exchange-polarization of the core s-electron wave functions by the unpaired d electrons.[14–18] The resultant slightly different radial variations of up- and down-spin s electrons in a given orbital leads to an unbalanced spin density at the nucleus. Summed over the 1s, 2s, and 3s shells the net contact interaction is equivalent to a large magnetic field at the nucleus:

$$H=AS_z/\mu_n\simeq 196S_z(\text{kgauss}) \tag{2}$$

for Fe^{57} in ZnO at room temperature. This value is 11% less than that found by Rosenvasser and Feher for Fe^{57} in MgO (octahedral oxygen coordination).[19] Both the magnitude of the equivalent field at the nucleus and

---

[9] G. W. Ludwig and H. H. Woodbury, Phys. Rev. **117**, 1286 (1959).

[10] W. Low, Proc. Phys. Soc. (London) **B69**, 1169 (1956).

[11] W. M. Walsh, Jr., Phys. Rev. **122**, 762 (1961).

[12] W. M. Walsh, Jr., J. Jeener and N. Bloembergen (unpublished data).

[13] R. G. Shulman and S. Sugano, Phys. Rev. Letters **7**, 157 (1961).

[14] J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957).

[15] V. Heine, Phys. Rev. **107**, 1002 (1957).

[16] R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960).

[17] D. A. Gooding and V. Heine, Phys. Rev. Letters **5**, 370 (1960).

[18] R. E. Watson and A. J. Freeman, J. Appl. Phys. **32**, 118S (1961).

[19] E. S. Rosenvasser and G. Feher, Bull. Am. Phys. Soc. **6**, 117 (1961).

its variation with host lattice correspond quite closely with those observed in the case of Mn^{55}: $170S_z$ kgauss in ZnO at room temperature, a 7% reduction with respect to MgO. This correlation is merely another example of the roughly constant polarizability of the core *s*-orbitals of the 3*d* ions which has been noted before.[15] Since, in the present experiment, we are unable to determine the sign of A for Fe^{57}, the analogy with Mn^{55} must be used to argue that it is very likely that A is negative, i.e., that the field at the nucleus is opposite to an applied external field which produces a net $\langle S_z\rangle$ on the Fe^{3+} ion.

Though the precise magnitude of the hyperfine coupling constant is of little value for a direct comparison with theory due to inherent difficulties in the latter[18] these numbers do permit us to say something concerning the sublattice magnetizations in yttrium-iron-garnet (YIG). Robert[20] has measured the nuclear magnetic resonance (NMR) frequencies, ν_{NMR}, of Fe^{57} in both the octahedral (*a*) and tetrahedral (*d*) sites of YIG. Assuming the contact interaction to be dominant (the contribution of the dipolar fields of neighboring ions is estimated to be on the order of a kilogauss) the resonance condition is

$$\nu_{\mathrm{NMR}}=A\langle S_z\rangle/h$$

where $\langle S_z\rangle$ is the average value of S_z for the ion. There is interest in determining the value of $\langle S_z\rangle$ for each sublattice at 0°K where spin-wave theory suggests that there may exist appreciable deviations from the ideal Néel state.[21] In order to evaluate $\langle S_z\rangle$ the appropriate values of A must be obtained. While one would prefer to measure A for traces of Fe^{57} in the diamagnetic isomorph to YIG, yttrium-gallium garnet (YGaG),[2] excessive linewidth and spectral interference make this direct determination extremely difficult. At present the best estimates of the A values may be obtained by correcting the measurements on $(Fe^{57})^{3+}$ in MgO and ZnO to the iron-oxygen distances appropriate to the *a* and *d* sites of YIG, respectively. This correction is quite unimportant in the case of the MgO-*a*-site conversion since the cation-anion distances differ by only 1.5% (1.98 Å in YIG *a* sites, 2.01 in MgO) and the volume sensitivity of the Mn^{55} hyperfine coupling is known to be small in this lattice[11] ($\partial \ln A/\partial \ln V=0.06$). The net effect is to decrease the magnitude of A by less than 0.3% which is well within the limits of error of the PMR experiment. The correction in the case of the tetrahedral *d* site is less trivial, however, since there is a significant difference in interionic spacing (1.98 Å in ZnO vs 1.88 Å in YIG *d* sites). The volume sensitivity of the hyperfine coupling is not known for this lattice but we estimate it to be roughly equal to that of Mn^{55} in ZnS ($\partial \ln A/\partial \ln V=0.35$),[11] since the temperature variations of the A for Mn^{55} in ZnO and ZnS are nearly identical.[22] As a result we estimate the value of A for Fe^{57} in the *d* sites of YIG to be reduced by roughly 5% to 8.57×10^{-4} cm^{-1}. The appreciable temperature dependence of the A for Mn^{55} in ZnO indicates that our room temperature value of A for Fe^{57} should be increased by about 1.4% in going to 0°K. The "final" *d*-site value is thus 8.70×10^{-4} cm^{-1}.

TABLE II. Numerical parameters related to the degree of sublattice alignment at 0°K in yttrium-iron garnet.

YIG site	ν_{NMR}[a] (Mc/sec)	A[b] (cm^{-1})	ν_{calc}[c] (Mc/sec)
octahedral (*a*)	76.5	10.1×10^{-4}	75.7
tetrahedral (*d*)	65.0	8.7×10^{-4}	65.2

[a] Experimental observations of reference 20.
[b] Estimated, as discussed in the text, from the data of reference 19 and the present experiment.
[c] Computed assuming $\langle S_z\rangle=5/2$, i.e., complete alignment.

It should be noted that these corrections must be made with some reservations since the presence of trivalent iron ions in divalent cation sites of the diamagnetic host crystals presumably reduces the local interionic spacing to an unknown extent so that the volume correction is of dubious accuracy and the effect of tighter binding is unknown. The latter may not be too significant in view of the parallel between $(Mn^{55})^{++}$ and $(Fe^{57})^{3+}$ mentioned above.

In Table II are given the 0°K NMR frequencies observed by Robert and the frequencies calculated from Eq. (2) using the values of A estimated as discussed above and assuming perfect sublattice alignment, i.e., $\langle S_z\rangle=\frac{5}{2}$. The agreement is within the ±2% experimental errors of the PMR data to which one should add the uncertainties in the conversions from one lattice to another. It is reasonable to conclude on the basis of this comparison that any reduction of the sublattice magnetizations in YIG at 0°K due to zero-point spin waves must be less than 2% and is very likely less than 1%.

ACKNOWLEDGMENTS

We are indebted to R. C. Linares for all of the samples used in these experiments. Dr. A. R. Hutson brought the Li compensation technique to our attention. Dr. G. K. Wertheim provided the Fe_2O_3 enriched in Fe^{57}. Miss B. B. Cetlin handled the numerical diagonalization using the program of Dr. S. Geschwind whose advice and encouragement have been appreciated in all phases of this work. A conversation with Dr. L. R. Walker greatly clarified the spin-wave picture.

---

[20] C. Robert, Compt. rend. **251**, 2684 (1960); **252**, 1442 (1961).

[21] L. R. Walker, J. Appl. Phys. **32**, 264*S* (1961).

[22] W. M. Walsh, Jr. (unpublished data).

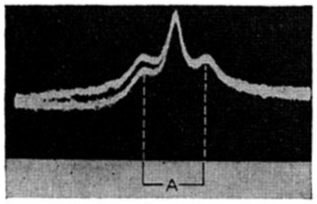

FIG. 4. The central transition of a sample doped with iron enriched to 60% in Fe^{57}. The hyperfine satellites are now resolved from the central Fe^{56} peak.